

The product was reduced quantitatively in a semimicro reduction apparatus using Adams, Voorhees and Shriner's platinum catalyst.¹⁰ The reductions were carried out at a pressure slightly greater than atmospheric. Fifty cubic centimeters of acetic acid was used as a solvent. The amount of catalyst was 0.2 g.

Sample, g.	Hydrogen abs. calcd. to standard cond., cc.	Mol. equiv. of abs. hydrogen	Time, min.
1 0.1984	39.3	2.88	60
2 .2005	41.7	3.04	160

Action of Sulfuric Acid on the Acetylenic Ketone.—A solution of 1 g. of the acetylenic ketone in 15 cc. of concentrated sulfuric acid was allowed to stand at room temperature for three hours. A deep red color developed. The solution was poured into a beaker of ice and the resulting mixture was extracted with ether. Three-tenths of a gram of colorless crystals was obtained by evaporating the ether and crystallizing the residue from methyl alcohol; m. p. 74–77°. This was identified as 2,4,6-trimethyldibenzoylmethane by a mixed melting point determination.

Benzoylmesitylacetylene.—A solution of 7.2 g. of mesitylacetylene in 25 cc. of absolute ether was added to 1.5 g. of sodium and the mixture refluxed for thirty minutes.

(10) Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, 1932, p. 452.

The contents of the flask were cooled to -15° and 18 g. of benzoyl chloride in 20 cc. of absolute ether was added all at once. The mixture was refluxed for one hour and again cooled. Enough 15% glacial acetic acid in absolute ether was added to dissolve the unchanged sodium. The resulting mixture was poured into 50 cc. of water; the ether layer was separated and shaken with 75 cc. of 10% sodium hydroxide solution for eight hours.

The ether solution was dried and divided into two portions. One of these was heated to drive off the ether and the residual oil was treated with semicarbazide. The semicarbazone melted at 170–172°. A mixed melting point with the semicarbazone of the original ketone (II) showed no lowering.

The second portion of the ether solution was evaporated to dryness and the residue recrystallized from alcohol. The benzoylmesitylacetylene obtained in this way melted at 68–70°. A mixture with II showed no lowering of the melting point.

Summary

Among the secondary products obtained by the interaction of phenylmagnesium bromide and β -methoxy- β -mesitylacrylonitrile is found a small amount of benzoylmesitylacetylene. Its structure has been established by degradation and by synthesis.

URBANA, ILLINOIS

RECEIVED DECEMBER 22, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Synthesis of Mixed Benzoin¹

BY REYNOLD C. FUSON, WILLIAM S. EMERSON² AND H. H. WEINSTOCK, JR.

There is considerable evidence to suggest that the hindrance provided by ortho substituents favors the tendency of a benzoin to exist as an ene-diol.³ To gain a more definite notion of the influence of hindrance on the properties of benzoin we have extended these studies to other highly hindered benzoin. The successful synthesis of hexamethylbenzoin by condensing mesitylglyoxal with mesitylene¹ suggested that mixed benzoin of this type might be made generally available. The present paper is a report of attempts to prepare these substances.

Mesitylglyoxal was first condensed with the series benzene, toluene, *m*-xylene and mesitylene in order to study the general synthesis under conditions of increasing hindrance. Carbon disulfide was used as the solvent in order to obtain

a standard set of conditions and to lessen the formation of diarylaroylmethanes. The time of the reaction was found to be very important. For benzene the reaction required twenty hours, for toluene six to ten and for *m*-xylene four to six hours. With shorter periods mesitylglyoxal hydrate was recovered, and with longer ones the product would not crystallize. The benzoin were identified by oxidation to the benzils either with sodium methylate and iodine in methyl alcohol⁴ or copper sulfate and pyridine.⁵

The yields of benzoin from benzene, toluene and *m*-xylene were 57, 24 and 17%, respectively. Mesitylene gave a 40% yield and the reaction was complete in one to one and one-half hours.

In the case of *m*-xylene 34% of 2,4,6-trimethylbenzoyldi-(2,4-dimethylphenyl)-methane was also obtained. Here the use of the carbon disulfide

(1) This is the third paper in this series. For the preceding paper see Arnold and Fuson, *This Journal*, **58**, 1295 (1936).

(2) Du Pont Post-Doctorate Fellow, 1937–1938.

(3) Weinstock and Fuson, *This Journal*, **58**, 1986 (1936).

(4) Corson and McAllister, *ibid.*, **51**, 2822 (1929).

(5) Clarke and Dreger, "Org. Syntheses," Coll. Vol. 1, 1932, p. 80.

solvent was very important, since the use of excess *m*-xylene as a solvent gave the diarylaroyl-methane as the sole product of the reaction.

The work was then extended to a study of 1,3,5-triethylbenzene, durene and isodurene. In no case could a benzoin be isolated. Either mesitylglyoxal hydrate was recovered or tars were obtained. Triethylbenzene would not react even when refluxed for five hours in ligroin at 90–95°.

In an effort to find a substituted benzene more reactive than the triethyl derivative and without the complication of a fourth group, 3,5-dimethyl-

After the reaction mixture had been decomposed with ice and hydrochloric acid the resulting emulsion was extracted twice with ether. The ether solution was washed once with water containing a little hydrochloric acid and then twice with water. After the solution was dried over anhydrous sodium sulfate the ether and carbon disulfide were distilled at reduced pressure. The residual oil was placed in an Erlenmeyer flask and petroleum ether evaporated from it by means of an air blast. A little petroleum ether was then added and the mixture set in the ice box to crystallize. The crude product was collected on a filter, washed with petroleum ether, dried and weighed. It was then crystallized from aqueous alcohol.

Products.—In the following table are summarized the products obtained.

Compound	M. p., °C.	Formula	Analyses, %					
			Calcd.		Found			
			C	H	C	H	C	H
2,4,6-Trimethylbenzoin	103.5–104.5 ⁸							
2,4,4',6-Tetramethylbenzoin	95–95.5	C ₁₈ H ₂₀ O ₂	80.6	7.47	80.4	80.6	7.31	7.41
2,4,4',6-Tetramethylbenzil ⁹	102.5–103	C ₁₈ H ₁₈ O ₂	81.2	6.77	81.0	81.1	6.92	6.92
2,2',4,4',6-Pentamethylbenzoin	120–120.5	C ₁₉ H ₂₂ O ₂	80.9	7.80	80.3	80.5	8.00	7.91
2,2',4,4',6-Pentamethylbenzil ⁹	84.5–85	C ₁₉ H ₂₀ O ₂	81.4	7.14	81.7	81.4	7.42	7.28
2,4,6-Trimethylbenzoyldi-(2,4-dimethylphenyl)-methane	146.5–147	C ₂₇ H ₂₀ O	87.6	8.11	87.4	87.6	8.19	8.29
2,2',4,4',6,6'-Hexamethylbenzoin	130.5–131 ¹⁰	C ₂₀ H ₂₄ O ₂	81.1	8.11	81.4	81.2	7.78	7.96
2,2',4,4',6,6'-Hexamethylbenzil ¹¹	122 ¹²							
2,4,6-Trimethylbenzoyldi-(2,4-dimethyl-6-methoxyphenyl)-methane ¹³	155.5–156.5	C ₂₉ H ₃₄ O ₃	81.0	7.91	80.95		7.84	
2,4,6-Trimethylbenzoyldi-(2,4-dimethyl-6-ethoxyphenyl)-methane	168–169	C ₃₁ H ₃₈ O ₃	81.20	8.30	81.25		8.22	

anisole and 3,5-dimethylphenetole were tried. These proved to be even more reactive than *m*-xylene. Even in carbon disulfide solution they condensed to give only the substituted diphenylbenzoylmethanes.

Experimental

Starting Materials.—Mesitylglyoxal was prepared by Arnold and Fuson's¹ modification of the method of Riley and Gray.⁶ 3,5-Dimethylanisole and 3,5-dimethylphenetole were made from 3,5-dimethylphenol by the procedure of Rowe, Bannister, Seth and Storey.⁷

Preparation of Benzoin.—All preparations and attempted preparations of benzoin were carried out in the same manner. In a 200-cc. three-necked flask equipped with a reflux condenser and drying tube, mercury-sealed stirrer and dropping funnel were placed 0.06 mole of anhydrous aluminum chloride, 0.03 mole of the hydrocarbon and about 70 cc. of carbon disulfide. This mixture was cooled with an ice-bath. The freshly distilled glyoxal (0.03 mole) in about 20 cc. of carbon disulfide was then added over a one-half to three-quarter hour period. The stirring was continued at 0° for a total of about six hours. In runs where the time was longer the ice-bath was allowed to warm up to room temperature after the first six hours at 0°.

(6) Riley and Gray, "Org. Synthesis," **15**, 67 (1935).

(7) Rowe, Bannister, Seth and Storey, *J. Soc. Chem. Ind.*, **49T**, 469 (1930).

Summary

Mesitylglyoxal has been condensed with benzene, toluene, *m*-xylene and mesitylene to yield the corresponding progressively hindered mixed benzoin.

Numerous attempts to condense mesitylglyoxal with tri- and tetrasubstituted aromatic hydrocarbons failed to yield the corresponding highly hindered mixed benzoin.

Mesitylglyoxal has been condensed with *m*-xylene, 3,5-dimethylanisole and 3,5-dimethylphenetole to give substituted diphenylbenzoylmethanes.

URBANA, ILLINOIS

RECEIVED DECEMBER 7, 1938

(8) Fuson, Weinstock and Ulyot [*THIS JOURNAL*, **57**, 1803 (1935)] give 102°.

(9) Prepared by oxidation of the corresponding benzoin by the method of Corson and McAllister.⁴

(10) Arnold and Fuson¹ erroneously reported the melting point of this compound as 59–60°.

(11) Prepared by oxidation of the benzoin by the method of Clarke and Dreger.⁵ This compound was identified by the mixed melting method with an authentic specimen made by the method of Fuson and Corse [*ibid.*, **60**, 2063 (1938)].

(12) Kohler and Baltzly, *ibid.*, **54**, 4015 (1932).

(13) This compound was accompanied by a substance melting at 185.5–186.5°. It had the composition of 2,4,6-trimethylphenyldi-(2,4-dimethyl-6-methoxyphenyl)-carbinol. *Anal.* Calcd. for C₂₉H₃₄O₃: C, 80.6; H, 8.34. Found: C, 80.54; H, 8.20.